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The present invention teaches amino alkoxylate organosilicone and their use, a preferred of which is as adjuvants for pesticides, as well intermediates for the manufacture of such siloxanes.

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Organosiloxane Containing Modified Groups in Pesticidal Compositions**Background of the Invention**

Many pesticides require the addition of an adjuvant to the spray mixture to provide wetting and spreading on foliar surfaces. Often that adjuvant is a surfactant, which can perform a variety of functions, such as increasing spray droplet retention on difficult to wet leaf surfaces, or to provide penetration of the herbicide into the plant cuticle. These adjuvants are provided either as a tankside additive or used as a component in pesticide formulations.

Gaskin, *et al.*, (*Pestic. Sci.* 1993, **38**, 185-192) demonstrated that some trisiloxane ethoxylates (TSE), such as Silwet L-77[®] surfactant (available from Witco Corp. of Greenwich, CT), can antagonize cuticular penetration of a herbicide into grasses, when compared to the herbicide alone. The term antagonism is used to indicate that the treatment of herbicide plus adjuvant is less effective than the comparative herbicide treatment.

Sandbrink, *et al.*, (*Pest. Sci.* 1993, **38**, 272-273) published that a TSE antagonized glyphosate performance relative to glyphosate alone in the control of *Panicum maximum* Jacq. Snow, *et. al.*, *Langmuir*, 1993, **9**, 424-30, discusses the physical properties and synthesis of novel cationic siloxane surfactants. These siloxanes are based on the reaction of a chloropropyl modified trisiloxane with an alkanolamine, such as N-methylethanolamine, which was further reacted with a halide to make a quaternary surfactant.

Petroff, *et al.*, (EP 92116658) describes the use of cationic, quaternary trisiloxanes to enhance the efficacy of glyphosate on velvetleaf, a broadleaf weed. Henning, *et al.*, (DE4318537) describes cationic siloxanyl modified polyhydroxy hydrocarbon or carbohydrate for use with plant protection agents. These 5 compounds are derived from a saccharide containing 1 to 10 pentose and/or hexose units, modified with a quaternary ammonium group, and a siloxane moiety. Reid, *et al.*, (USP 3,389,160) describes amino modified siloxane alkoxylates where the amino functionality appears as the terminal group on the alkyleneoxide moiety, opposite the siloxane group. Policello in PCT WO 10 97/32475 discloses amino modified siloxanes wherein the amine is bound by an ether bond to the siloxane backbone wherein the amine may be terminal or pendant to the backbone.

Dietz et al. in US Patent No. 5,891,977 describes organopolysiloxanes comprising polyhydroxyorganyl radicals and polyalkylene radicals, their process 15 and use. Specifically these materials are described as being useful in coatings, paints and inks, as well as emulsifiers for water-in-oil and oil-in-water systems, such as hair care formulations. Although these materials are mentioned as being practical for many applications, these were not shown to have utility as adjuvants for pesticidal applications.

20

Summary of the Invention

Organosiloxanes for use with pesticidally active compositions and those with utility in pesticide formulations to treat plants and animals are those

substituted with at least one aminealkoxylate group, which are novel siloxane structures. Intermediates for the manufacture for said siloxane are also disclosed herein.

5 **Detailed Description of the Invention**

The amino alkoxylate organosiloxanes described herein are useful as adjuvants for pesticide formulations, including but not limited to applications which may be used to treat plants or animals. The pesticidal formulations include (a) at least one modified organosiloxane; and (b) at least one pesticidally active component, but may contain optional ingredients.

(A) ORGANOSILOXANES

Preferably, the modified organosiloxanes of the present invention have the average general formula:



wherein f is between 0 to 50, preferably 1 to 5, more preferably 1 to 2, most preferably 1, d = 0 to 2, most preferably 0, e = 0 to 3, most preferably 0, if the siloxane is not cyclic, g = 2 + e + 2d, and if the siloxane is cyclic g = 0 and f \geq 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic
20 and Q is either an amino alkoxylate of the formula -BN[BO(C_aH_{2a}O)_bR¹]_{2-z}T_z or R², with at least one Q not being R², each a is 2 to 4, preferably 2 to 3, each b is 2 to 15, preferably 2 to 8, each B is a divalent bridging group of C1 to C8, preferably C3 to C4, each optionally OH substituted, z = 0 to 1, preferably 0, R¹ is

hydrogen or a hydrocarbon radical of 1 to 4 carbons, R² is either a polyether of the structure -BO(C_aH_{2a}O)_cR¹, hydrogen, an alkyl radical containing 1 to 18 carbons, preferably methyl, c is 0 to 15, and T is a univalent organic moiety.

Preferably most R² groups are methyl, but some may be polyethers of the structure -B(C_aH_{2a}O)_bR¹ as defined above, e.g., -C₃H₆(C₂H₄O)₈OH and -C₃H₆(C₂H₄O)₆(C₃H₆O)₂OCH₃. Exemplary B are -(CH₂)₂-, -(CH₂)₃-, and -CH₂CH(OH)CH₂- and -CH₂C₆H₉(OH)CH₂- Examples of R¹ are -H, and -CH₃.

Most preferably all Q groups which are terminal are methyl and there is at least one amino alkoxylate pendant, though alternatively, the terminal groups may be amino alkoxylates and the pendant Q groups may all be methyl. A particularly preferred siloxane is a (CH₃)₃SiOSiCH₃(Q)OSi(CH₃)₃ wherein the Q is an amino alkoxylate.

Preferably a is such that there is a mixture of ethylene oxide (EO), propylene oxide (PO) units and butylene oxide (BO) units. Preferably, for aqueous applications, there is a preponderance of EO units, most preferably every a = 2. For non-aqueous applications, such as crop oil concentrates, there may be more PO and BO units. When Q contains a mixture of oxyalkylenes, it may be blocked or random. One skilled in the art will understand the advantages in the position of the oxyethylene relative to the oxypropylene, when the alkyleneoxide group is blocked.

T groups preferably are alkyls (which may be branched, linear or cyclic) of less than 8 carbons. Another preferred T is an alkyl amine functionality, -BNR², which may be further substituted (e.g., with an alkyl) or be further alkoxylated,

e.g., -BN(C_aH_{2a}O)_cR¹. Alternatively, T may be an amino alkyl siloxane or an amino alkyl hydroxy siloxane, e.g., -B-N-B-(SiO_{1/2}R⁶)-X¹ wherein X¹ is a siloxane per formula I above (with the -B-N-B-(SiO_{1/2}R⁶)-X¹ group being taken as [O_yMeSi(Q)O_y] or [O_ySiMe₂Q]) and R⁶ is O_{1/2} or -CH₃. If T contains a siloxane, it 5 preferably is the same backbone as the siloxane to which Q is attached.

The Q groups may include protonated amines, i.e, where there is a hydrogen ion attached to the nitrogen in the Q group, which can occur to the aminosilicone alkoxylates under acidic conditions. Also contemplated herein are quaternary versions of Q, i.e., where there is a third T group on the nitrogen in 10 Q, but said quaternary compounds are not preferred for use in the present invention since they would tend to be phytotoxic.

Preferred Q structures are wherein R⁴ is hydrogen or methyl, a is 2, and b is from 4 to 6. Specific Q groups are -C₂H₄N[C₂H₄O(EO)₅CH₃]₂; -C₂H₄N[C₂H₄O(EO)₆H]₂; -C₃H₆N[C₃H₆O(EO)₃(PO)₂H](C₂H₅); 15 -C₃H₆OCH₂CH(OH)CH₂N[C₂H₄O(EO)₆H]₂; -C₃H₆OCH₂CH(OH)CH₂NH[C₃H₆O(EO)₆H]; -C₃H₆C(CH₃)₂N(C₂H₅)[C₃H₆O(PO)₅H]; -C₃H₆OCH₂(OH)CH₂NHC₃H₆O(EO)₂CH₂CH(CH₃)NHC₂CH(OH)CH₂OC₃H₆SiO_{2/2}((CH₃)₃SiO_{1/2})₂; and -C₃H₆O(C₂H₄O)₄CH₂CH(OH)CH₂N[CH₂CH₂O(EO)₄H]₂.

Preferred aminosilicone alkoxylates are trisiloxanes with R⁵ being methyl, with 20 B preferably being a C1 to C4 alkylene, most preferably propylene or 2-hydroxy propylene.

PESTICIDES

The pesticidal compositions of the present invention also include at least one pesticide, especially acid functionalized ones, i.e., compounds that contain at least one carboxylic, sulfonic or phosphonic acid group or their salt or ester. The term pesticide means any compound used to destroy pests, e.g., rodenticides, fungicides, and herbicides. Illustrative examples of pesticides which can be employed include, but are not limited to, growth regulators, photosynthesis inhibitors, pigment inhibitors, mitotic disrupters, lipid biosynthesis inhibitors, cell wall inhibitors, and cell membrane disrupters. The amount of pesticide employed in compositions of the invention varies with the type of pesticide employed. More specific examples of pesticide compounds that can be used with the compositions of the invention are: phenoxy acetic acids, phenoxy propionic acids, phenoxy butyric acids, benzoic acids, triazines and s-triazines, substituted ureas, uracils, bentazon, desmedipham, methazole, phenmedipham, pyridate, amitrole, clomazone, fluridone, norflurazone, dinitroanilines, isopropalin, oryzalin, pendimethalin, prodiame, trifluralin, glyphosate, sulfonylureas, imidazolinones, clethodim, diclofop-methyl, fenoxaprop-ethyl, fluazifop-p-butyl, haloxyfop-methyl, quizalofop, sethoxydim, dichlobenil, isoxaben, and bipyridylum compounds.

The pesticide may be a liquid or a solid. If a solid, it is preferable that it is soluble in a solvent prior to application, and the silicone may act as a surfactant for such solubility or additional surfactants may perform this function.

It is preferable that the pesticide be one that is other than a solvent. For example, it is preferable that the pesticide do not include solvents which have also at times been categorized as being pesticidally active compounds. Such solvents include paraffinics; oils including animal, mineral, vegetable, silicone, 5 and so forth; fatty acids, esters, and amides of fatty acids; alkanes; ketones; alcohols; glycols; alkyl/aryl alkoxylates; diols; acetates; and so forth.

EXCIPIENTS

Buffers, preservatives and other standard excipients known in the art also 10 may be included in the composition. When the compositions of the present are insoluble in distilled water, spreading may be achieved by the addition of a small amount of an acid, such as acetic acid, to protonate the amine functionality, thereby increasing water solubility.

Solvents may also be included in compositions of the present invention. 15 These solvents are in a liquid state at room temperature. Examples include water, alcohols, aromatic solvents, oils (i.e. mineral oil, vegetable oil, silicone oil, and so forth), lower alkyl esters of vegetable oils, fatty acids, ketones, glycols, polyethylene glycols, diols, paraffinics, and so forth. Particular solvents would be 2, 2, 4-trimethyl, 1-3-pentane diol and alkoxylated (especially ethoxylated) 20 versions thereof, See US Patent No. 5,674,832 to Keyes, or n-methyl-pyrrilidone.

Moreover, other cosurfactants, which have short chain hydrophobes which do not interfere with superspreading may be included. See US Patent No. 5,558,806 to Policello et al., which is incorporated by reference.

The cosurfactants useful herein include nonionic, cationic, anionic,

5 amphoteric, zwitterionic, polymeric surfactants, or any mixture thereof.

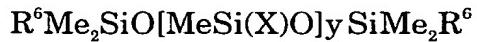
Surfactants are typically hydrocarbon based, silicone based or fluorocarbon based.

Useful surfactants include alkoxylates, especially ethoxylates, containing block copolymers including copolymers of ethylene oxide, propylene oxide, 10 butylene oxide, and mixtures thereof; alkylaryllalkoxylates, especially ethoxylates or propoxylates and their derivatives including alkyl phenol ethoxylate; arylarylalkoxylates, especially ethoxylates or propoxylates, and their derivatives; amine alkoxylates, especially amine ethoxylates; fatty acid alkoxylates; fatty alcohol alkoxylates; alkyl sulfonates; alkyl benzene and alkyl naphthalene sulfonates; sulfated fatty alcohols, amines or acid amides; acid 15 esters of sodium isethionate; esters of sodium sulfosuccinate; sulfated or sulfonated fatty acid esters; petroleum sulfonates; N-acyl sarcosinates; alkyl polyglycosides; alkyl ethoxylated amines; and so forth.

Specific examples include alkyl acetylenic diols (SURFONYL-Air Products), pyrrolidone based surfactants (e.g., SURFADONE - LP 100 - ISP), 2-ethyl hexyl sulfate, isodecyl alcohol ethoxylates (e.g., RHODASURF DA 530 - Rhodia), ethylene diamine alkoxylates (TETRONICS - BASF), and ethylene

oxide/propylene oxide copolymers (PLURONICS – BASF) and Gemini type surfactants (Rhodia).

Preferred surfactants include ethylene oxide/propylene oxide copolymers (EO/PO); amine ethoxylates; sorbitol ethoxylates; and so forth. The optional 5 silicone surfactants include trisiloxane alkoxylates (TSAs) of the general formula:



wherein y = 0 to 2, preferably 1, X is as above, and R⁶ is G, or an alkyl of one to four carbons. The preferred nonionic siloxane alkoxylates are trisiloxane

10 alkoxylates, where y = 1, a = 3, q = 4 to 8, r = 0, R⁶ is Me, R³ is H or Me.

A suspension aid is preferably utilized if a pesticide concentrates is made with the modified siloxanes to improve physical stability.

MANUFACTURE OF SILOXANES

15 The amine modified organosiloxanes of the present invention may be made by the hydrosilation of a hydridosiloxane with an epoxy intermediate, such as allyl glycidal ether, vinyl cyclohexene monoxide, or an epoxy terminated allyl polyalkyleneoxide, followed by ring opening the epoxide with the appropriate amino alkoxylate group. The hydridosiloxanes described are commercially 20 available and may be made as known in the art. Hydrosilation conditions depend on the reactants, but are within the general conditions taught in Marciniec (*Comprehensive Handbook of Hydrosilylation*, Edited by Bogdan Marciniec, Pergamon Press).

Epoxy terminated, allyl polyethyleneoxide can be prepared by the method outlined by Xue-Ping Gu, *et al*, (Synthesis of Glycol Diglycidyl Ethers Using Phase-Transfer Catalysis; in *Synthesis Communications June / July 1985*, p. 649-651) from an epoxide and commercially available allyl started polyalkylene oxides.

Amino alkoxylates which are to be reacted with the epoxide may be terminated with an alkyl or hydroxyl or may be terminated with an amine, so that the alkoxylate is a diamine. Such diamines are available under the tradename JEFFAMINE. In such a case the diamine would crosslink many of the siloxanes, thus, it is preferable to use with diamines siloxanes with only one epoxy functionality per molecule. The resulting product would be two siloxane chains linked by an amino alkoxylate amino bridge. Short chain siloxanes, e.g., trisiloxanes would be preferable for same.

Alternatively to make the amine modified siloxanes one may start from the reaction product of an allyl or methallyl chloride and an alkoxylated amine compound and hydrosilate this allylic polyhydric amine onto hydridosiloxanes. Hydrosilation conditions depend on the amine and siloxane, but again are within the general conditions taught in Marciniec.

If a siloxane is a terpolymer, i.e., has two different functionalities hydrosilated onto the backbone (e.g., an amino alkoxylate, polyether siloxane) such hydrosilations may be done sequentially or at the same time depending upon the reactivities of the species to be hydrosilated, as well as the desired end-

product. The reaction conditions for hydrosilating an allyl started polyether are well known in the art.

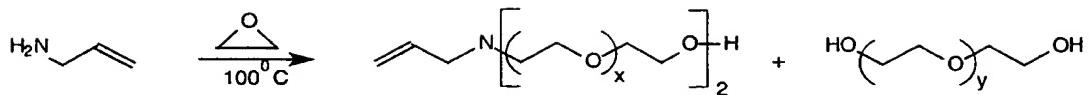
The alkenylamino polyalkyleneoxides intermediate structures to be reacted with the hydridosiloxanes are of the formula $B'N[BO(C_aH_{2a}O)_bR^1]_{2-z}T_z$

5 wherein all formulae as are above, except B' is an alkenyl, with an α , β unsaturation at the end of the alkenyl opposite from the nitrogen atom. The alkenyl could be C1-C18, preferably C1-C6, and most preferably allyl or methallyl. To make this alkenyl amine alkoxylate, an alkenyl salt, e.g., allyl bromide, is reacted with ammonia, or a secondary or primary amine. This amine

10 product then is alkoxylated.

An exemplary alkoxylation procedure would be as follows (with chemistry noted below)- Charge allyl amine to reactor. Degas and pressurize with nitrogen. Heat to 105°C, and then add 25 psig (.0015 N²/m) of nitrogen above the pressure exerted by allyl amine. Gradually add EO, to maintain temperature below 115 C, and pressure below 80 psig (.0095 N²/m). The formation of the tertiary amine will cause a great drop in the reactor pressure, at this time continual addition of EO could proceed at 105-110°C and a pressure range of 60 - 80 psig (0.0066 to 0.0095 N²/m). After the required amounts of EO is added, the reaction is allowed to digest for 30 minutes, residual EO is removed by vacuum, the reactor is cooled, and the product removed by slight pressurization of the reactor.

Any glycol's which may have been produced due to utilization of a partially wet amine may be stripped by vacuum.



The allyl amino polyalkyleneoxides also may be prepared by reaction of an allyl glycidyl ether (or similar unsaturated epoxide) with an amine alkoxylate (which result in an ether bond). If a diamine is used for such a reaction, a 5 diallylic species will be formed, which will act as a crosslinker and preferably should be used with a mon-hydridosiloxane. An alternative method uses aziridine, which is not preferred for toxicity reasons, are disclosed in PCT US97/04128, which is incorporated herein by reference.

10 The nonionic siloxane and the pesticides are commercially available and their manufacture is known in the art.

USE

The modified organosiloxanes may be used in agricultural applications as adjuvants for pesticides wherein the siloxane is applied in a pesticide 15 formulation to agricultural products or to treat animals. The composition of the present invention is useful as a tank side additive in an animal shampoo, or as a component in a herbicide formulation. In addition the compositions of the present invention are useful as adjuvants for other pesticides, such as, fungicides, insecticides, plant growth regulators, acaracides and the like. The 20 pesticide formulations may be wet, dry, slurries or other formulations as are known in the art.

The siloxanes are added directly to a spray tank along with an acid functional pesticide, or as part of a pesticide formulation. When used as a tankside additive, the siloxane is present at weight concentrations between 0.001% and 5.0%, preferably between 0.025% and 0.5%. Likewise, when the 5 modified organosiloxanes are used in a pesticide formulation (In-can), they are present at weight concentrations that will deliver between 0.001% and 5.0% to the final use dilution, preferably between 0.025% and 0.5%, of the final use dilution.

It is noted that most dilutions will be made with water, but in the case of 10 crop oil concentrates, oils (mineral, silicone, animal or vegetable oils) will be the diluents.

When the compositions of the present invention are used in conjunction with a TSA, the weight ratio of the TSA to the modified organosiloxanes is between 5:95 and 95:5, preferably between 5:95 and 40:60. The blend may be 15 accomplished by mixing physically the two components prior to use, or by adding them separately to a spray mixture at the point of use.

When the compositions of the present invention are used in conjunction with nonsilicone surfactants, the weight ratio of the nonsilicone surfactant to the modified organosiloxane is between 1:99 and 99:1, preferably between 99:1 and 20 40:60.

Additionally, the amino alkoxylate organosiloxanes also may be used generally as surface active agents in aqueous formulation where there is an acid functionalized component. These organosiloxanes also may be used as surface

active agents, including, but not limited to, as surfactants, wetting agents and softeners for textiles, flow and leveling agents in coatings, hair care products, skin care and creams for personal care applications and anti-static agents, detergents and softeners for laundry products.

5

Examples

Unless otherwise indicated, all parts and percentages are by weight, and are based on the weight at the particular stage of the processing being described.

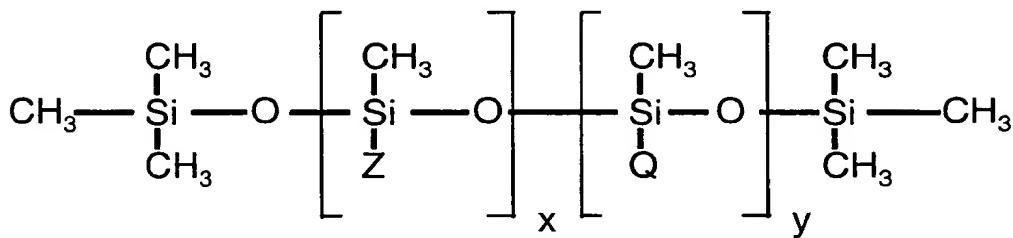
Example 1 - Alkoxylation of Allyl Amine

To a two liter Parr pressure reactor was charged 200.4 g of allyl mine.

The reactor was heated to 60°C, which resulted in a pressure of 10 psig. To the system was added 25 psig of nitrogen, and 50 g of EO. The reactor was heated
10 gradually until an exotherm was noticed. This occurred at 103°C and caused a pressure jump to 105 psig. After the reaction subsided the temperature was kept at 103 and more EO added between 40 - 60 psig. After approximately 100 g was added another exotherm occurred to 130°C and caused a raise in pressure to 70 psig. After this exotherm subsided the reaction behaved very well and
15 continuous addition of EO was possible. Catalysis after the formation of a tertiary amine was not required for subsequent addition of EO. The temperature range of the reaction was 103 -110°C, with a pressure of range of 40 - 45 psig (including 25 psi of Nitrogen), and a rate of addition of 20-25 g/min. of EO.

Example 2

Aminosilicone alkoxylates were prepared by the slow addition of the desired allyl amino polyalkyleneoxide to a reaction vessel containing heptamethyltrisiloxane (in a 1.3:1 mole ratio). Therefore, 25.7g of 5 heptamethyltrisiloxane (0.1155 moles), 39.3g of allylamine ethoxylate, 4.6 EO, (0.1501 moles), along with 30 g isopropanol (solvent) were weighed into a 250 mL roundbottom flask equipped with an addition funnel, reflux condenser and an overhead stirrer. The flask contents were heated to 65°C and catalyzed with 0.3 g of potassium trichloro-ethylene platinate (III) solution (1% in isopropanol) and 10 held at this temperature for 6 h. The reaction mixture was heated to 75 °C , and an additional 0.56 g of catalyst solution was added. The reaction mixture was maintained at this temperature for an additional 5 hours at which time another 0.26 g of catalyst solution was added to the reaction mixture, and stirred for an 15 additional hour. The reaction was monitored by introducing a sample of the reaction mixture into a fermentation tube containing KOH/water/ethanol solution. The generation of hydrogen indicates an incomplete reaction. The flask contents were mixed until the SiH intermediate was consumed. The mixture was cooled to 45 °C, filtered through a fine filter pad, and stripped on a Rotovap for 1.5 hours at 70°C and 1.0 mm Hg to yield a dark amber colored 20 product with a viscosity of 78 cps (Spindle LV-3 @ 100 rpm), a refractive index of 1.4520 (25°C) and an aqueous surface tension of 21.1 mN/m (0.1 wt%, Wilhelmy Plate). The resulting aminosilicone alkoxylate is shown in Table 1.

Table 1**Description of Modified Organosiloxanes**

5

<u>Reference</u>	<u>x</u>	<u>y</u>	<u>Description</u>
MSIL-1	0	1	$\text{Q} = \text{C}_2\text{H}_4\text{N}[(\text{C}_2\text{H}_4\text{O})_a\text{H}_3]_2$, where $a = 4.6$

Example 3

10 This example demonstrates the utility of the organosilicone composition of the present invention as a surfactant. Aqueous solutions of this siloxane provided a significant reduction in surface tension relative to water. Surface tension was measured using a Cahn microbalance, with a sand blasted platinum blade as the sensor. Solutions of the various components were prepared at 0.1
 15 wt% in 0.005M NaCl water (Deionized), as an equilibrium aid.

Spreading was determined by applying a 10 μL droplet of surfactant solution to a polyester film (3M, IR 1140 transparency film) and measuring the spread diameter after 30 seconds. The solution was applied with an automatic pipette to provide droplets of reproducible volume. Deionized water that was

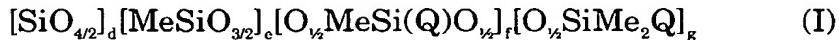
further purified with a Millipore filtration system was used to prepare the surfactant solutions.

Table 2 - Comparison of Aqueous Surface Tension Properties

<u>Surfactant</u>	<u>Surface Tension (mN/m)</u>	<u>Spread Diameter (mm)</u>	
		<u>0.1 wt%</u>	<u>0.2 wt%</u>
MSIL-1	21.1	27	34
a. Surface tension in mN/m at 25°C.			
b. Surface tension of water from <u>CRC Handbook of Chemistry and Physics</u> ; 63 Edition, 1982-1983.			
* Spread diameter of distilled water = 4 mm			

We claim:

1. A modified organosiloxanes of the present invention have the average general formula:

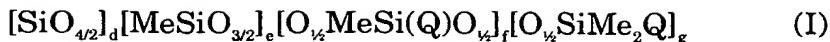


5 wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an amino alkoxylate of the formula -BN[BO(C_aH_{2a}O)_bR¹]_{2-z}T_z or R², with at least one Q not being R², each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging 10 group of C1 to C8, each optionally OH substituted, z = 0 to 1, R¹ is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R² is either a polyether of the structure -BO(C_aH_{2a}O)_cR¹, hydrogen or an alkyl radical containing 1 to 18 carbons, c = 0 to 15, and T is a univalent organic moiety.

2. A composition according to claim 1 wherein T is an alkyl (which may be 15 branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, -BNR¹₂, or B-N-B-(SiO_{1/2}R⁶)-X¹ wherein X¹ is a siloxane per formula I and R⁶ is O_{ν_4} or -CH₃.

3. A composition according to claim 1 wherein f = 1 to 5, d = 0, e = 0 and 20 g = 2.

4. A composition according to claim 1 additionally comprising a pesticide.
5. A composition according to claim 3 wherein T is an alkyl and z = 1.
6. A process for applying a pesticide comprising applying to an animal or plant a composition comprising:



wherein f is between 0 to 50, d = 0 to 2, e = 0 to 3, if the siloxane is not cyclic, g = 2 + e + 2d, if the siloxane is cyclic, g = 0 and f ≥ 1, e+d+f+g = 2 to 50 if the siloxane is non-cyclic and = 4 to 8 if the siloxane is cyclic and Q is either an amino alkoxylate of the formula -BN[BO(C_aH_{2a}O)_bR¹]_{2-z}T_z or R², with at least one Q not being R², each a is 2 to 4, each b is 2 to 15, each B is a divalent bridging group of C1 to C8, each optionally OH substituted, z = 0 to 1, R¹ is hydrogen or a hydrocarbon radical of 1 to 4 carbons, R² is either a polyether of the structure -BO(C_aH_{2a}O)_bR¹, hydrogen or an alkyl radical containing 1 to 18 carbons and T is a univalent organic moiety.

7. A process according to claim 6 additionally comprising applying a cosurfactant.

8. A process according to claim 6 wherein f = 1 to 5, d = 0, e = 0 and g = 2 and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, -BNR¹₂, or B-N-B-(SiO_{1/2}R⁶)-X¹ wherein X¹ is a siloxane per formula I and R⁶ is O_{1/2} or -CH₃.

9. An amine of the formula B'N[BO(C_aH_{2a}O)_bR¹]_{2-z}T_z wherein B' is an alkenyl, with an α, β unsaturation at the end of the alkenyl opposite from the nitrogen atom, a = 2 to 4, b = 2 to 15, z = 1 to 2, B is a divalent bridging group of C1 to C8, each optionally OH substituted, R¹ is hydrogen or a hydrocarbon radical of 1 to 4 carbons and T is an alkyl (which may be branched, linear or cyclic) of less than 8 carbons, an alkyl amine functionality, or -BNR¹₂.

10. An amine according to claim 9 wherein z = 0.

M.H

**PATENT COOPERATION TREATY
PCT**

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SIL0034	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/US 99/ 22490	International filing date (<i>day/month/year</i>) 27/09/1999	(Earliest) Priority Date (<i>day/month/year</i>) 28/09/1998
Applicant CK WITCO CORPORATION et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
 - the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
 - contained in the international application in written form.
 - filed together with the international application in computer readable form.
 - furnished subsequently to this Authority in written form.
 - furnished subsequently to this Authority in computer readable form.
 - the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
 - the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
- 2. **Certain claims were found unsearchable** (See Box I).
- 3. **Unity of invention is lacking** (see Box II).
- 4. With regard to the **title**,
 - the text is approved as submitted by the applicant.
 - the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

- the text is approved as submitted by the applicant.
- the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

- as suggested by the applicant.
- because the applicant failed to suggest a figure.
- because this figure better characterizes the invention.

None of the figures.

INTERNATIONAL SEARCH REPORT

Int'l. Appl. No.
PCT/US 99/22490

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G77/388 C08G77/46 C08G65/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 404 698 A (RHONE-POULENC) 27 December 1990 (1990-12-27) page 5, line 43 - line 47 example 1 claim 1 ---- EP 0 535 596 A (DOW CORNING) 7 April 1993 (1993-04-07) cited in the application page 4, line 8 - line 16 examples 1,9,10 page 4, line 25 - line 29 claims ---- -/-	1-8
Y		6-8

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

4 February 2000

Date of mailing of the international search report

16/02/2000

Name and mailing address of the ISA

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Hoepfner, W

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 99/22490

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 198332 Derwent Publications Ltd., London, GB; AN 1983-732235 XP002129810 & JP 58 111893 A (DAIICHI KOGYO SEIYAKU CO. LTD.) abstract --- -----	9,10
Y		1-5
A	WO 97 32475 A (G. A. POLICELLO) 12 September 1997 (1997-09-12) cited in the application examples 1-3 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 99/22490

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 404698	A	27-12-1990	FR	2648821 A	28-12-1990
			JP	3095228 A	19-04-1991
			JP	5081609 B	15-11-1993
			US	5075403 A	24-12-1991
			US	5147578 A	15-09-1992
EP 535596	A	07-04-1993	AU	2539992 A	01-04-1993
			JP	5238910 A	17-09-1993
			MX	9205534 A	01-03-1993
JP 58111893	A	04-07-1983	NONE		
WO 9732475	A	12-09-1997	AU	2213097 A	22-09-1997
			BR	9707913 A	27-07-1999
			CA	2247963 A	12-09-1997
			EP	0892602 A	27-01-1999

PATENT COOPERATION TREATY

PCT

REC'D 06 NOV 2000

WIPO

PCT

9

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference W32.3-8901	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US99/22490	International filing date (day/month/year) 28/09/1999	Priority date (day/month/year) 28/09/1998
International Patent Classification (IPC) or national classification and IPC C08G77/388		
<p>Applicant CROMPTON CORPORATION et al.</p> <p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 9 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p> <p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input checked="" type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input checked="" type="checkbox"/> Certain defects in the international application VIII <input checked="" type="checkbox"/> Certain observations on the international application 		

Date of submission of the demand 28/04/2000	Date of completion of this report 02.11.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Ammendola, P Telephone No. +49 89 2399 8662



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US99/22490

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-17 as originally filed

Claims, No.:

1-10 as originally filed

2. The amendments have resulted in the cancellation of:

- the description, pages:
 the claims, Nos.:
 the drawings, sheets:

3. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

III. Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

The questions whether the claimed invention appears to be novel, to involve an inventive step (to be non-obvious), or to be industrially applicable have not been examined in respect of:

- the entire international application.
 claims Nos. 6-8 (Industrial Applicability).

because:

- the said international application, or the said claims Nos. 6-8 relate to the following subject matter which does not require an international preliminary examination (*specify*):

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/US99/22490

s s parat sheet

- the description, claims or drawings (*indicate particular elements below*) or said claims Nos. are so unclear that no meaningful opinion could be formed (*specify*):

- the claims, or said claims Nos. are so inadequately supported by the description that no meaningful opinion could be formed.

- no international search report has been established for the said claims Nos. .

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-8
	No:	Claims 9,10
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-8
Industrial applicability (IA)	Yes:	Claims 1-5,9,10
	No:	Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separat she t

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/22490

Reference is made to the following documents:

- D1: WO 97 32475 A (G. A. POLICELLO) 12 September 1997 (1997-09-12) cited in the application
- D2: DATABASE WPI Week 198332 Derwent Publications Ltd., London, GB; AN 1983-732235 XP002129810 & JP 58 111893 A (DAIICHI KOGYO SEIYAKU CO. LTD.)
- D3: EP-A-0 535 596 (DOW CORNING) 7 April 1993 (1993-04-07) cited in the application.

Re Item III

Non-establishment of opinion with regard to novelty, inventive step and industrial applicability

1. Claims 6-8 relate to subject-matter considered by this Authority to be covered by the provisions of Rule 67.1(iv) PCT. Consequently, no opinion will be formulated with respect to the industrial applicability of the subject-matter of these claims (Article 34(4)(a)(i) PCT).

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

2.a NOVELTY (Article 33(2) PCT)

i) It is evident from p.5/15-18, p.12/2-8 that the alkenyl "B'" group in the formula of claim 9 may comprise ether bonds. Since, claim 9 does **not** limit at all the nature of the "B'" groups (see the definition of "B'" in present claim 9, but also item "4.c" here after) the amines mentioned at p.10 of D1 are novelty destroying for claim 10. Moreover, D2 discloses the alkenyl-amine polyether obtained by reacting ethylene oxide with allylamine. Therefore, the subject-matter of claim 10 is anticipated also from D2.

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International application No. PCT/US99/22490

ii) Claim 9 includes amines according to the given formula with "z=2". Amines according to such formula (which do not carry any polyether pendant) are conventional (see, e.g. N,N-dimethylallylamine). Therefore, the subject-matter of present claim 9 is not novel (Article 33(2) PCT).

It seems that the feature "z = 1 to 2" in claim 9 is the result of a typing error and that claim 9 was intended to define "z = **0 to 1**" (see item "4.a" here after). If this assumption is correct, then D1 and D2 would be novelty destroying also for claim 9.

iii) None of the available documents discloses modified polysiloxanes carrying amines with polyether pendants, wherein **not more than 8 carbons** are present in the group bridging the N atom to the Si. Obviously, also the claimed process involving such novel modified polysiloxanes is novel.

Therefore the subject-matter of claims 1-8 satisfies the requirements of Article 33(2) PCT.

2.b INVENTIVE STEP (Article 33(3) PCT)

The present application does not satisfy the criterion set forth in Article 33(3) PCT because the subject-matter of claims 1-8 does not involve an inventive step (Rule 65(1)(2) PCT).

It is evident from p.5/15-18 and p.12/2-8 of the description that the "B" bridging group in the organosiloxane may comprise ether bonds.

Therefore, the **only** feature distinguishing the organosiloxanes of claim 1 modified by the groups mentioned at p.5/15-19 (wherein one or more ether groups are present along the "B" segment deriving from the alkenyl) is in that the **total** number of carbon atoms is **at most 8**, while in the corresponding portions of the organosiloxanes **explicitly** mentioned in D1 (see p.10 CATSII 1) the number of carbon atoms is at least 9.

In the absence of convincing evidence (such as experimental comparison between the properties of the claimed organosiloxanes with a "B" group defined at p.5/18 and that of D1 indicated as "CATSIL 1" in Table of D1) showing that a certain technical effect is **only** obtainable when the number of carbon atoms is **not more than 8**, the only objective problem solved by the present application may be regarded as that of providing an alternative to the organosiloxanes defined in D1.

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International application No. PCT/US99/22490

This problem has been solved by making a **selection within** the overall teachings of D1 (the formula given for "Z" in claim 1 of D1 embraces also the case in which R¹ and R² are both C2 and n =1 when R¹=C3, or n=2 when R¹ = C2, i.e. Z groups may contain as low as 7 or 8 carbon atoms in the group bridging the N to the Si) or in immediately contiguous structural alternatives. Therefore, no inventive step may be recognised for the subject-matter of present claims 1-8.

With respect to the portion of claimed matter of claims 1-8 wherein the " B " groups do not comprise any ether group, i.e. is an hydrocarbon with at most 8 carbon atoms (see the formulae disclosed at p. 5/13-14 and all the invention examples), it must be stressed that the applicant could in principle limit the claimed matter of present claims 1-8 to such bridging groups (this would imply **deletion of p.5/15-18 and of p.12/2-8 of the description and indication of "hydrocarbon" before "divalent" and "alkenyl" in claims 1, 6 and 9). However, the closest state of the art for such organosiloxanes containing **no ether bond** in the groups bridging the Si to the N would be represented by D3 (see D3 claims and p.4/8-11). It is obvious for the skilled reader of D3, searching for a solution to the problem of providing an alternative to the organosiloxanes modified with **quaternized** amines used in D3, to find D1 disclosing the use with pesticides of organosiloxanes functionalised with **alkoxy** amines. Therefore, even the portion of matter claimed in claims 1-8 referring exclusively to organosiloxanes wherein the " B " groups **do not** comprise any ether group, is not inventive in view of D3 in combination with D1.**

2.c INDUSTRIAL APPLICABILITY

Claim 6 defines processes which are medical treatments of animals.

Therefore, for the assessment of the present claims 6-8 on the question whether they are industrially applicable, no unified criteria exist in the PCT Contracting States.

The patentability can also be dependent upon the formulation of the claims. The EPO, for example, does not recognize as industrially applicable the subject-matter of claims to the process corresponding to a medical treatment, but may allow, however, claims to a known compound for first use in a medical treatment and the use of such a compound for the manufacture of a medicament for a new medical treatment.

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/US99/22490

Re Item VII

Certain defects in the international application

3.a The units "psig" expressed on p.14 do not meet the requirements of Rule 10.1 PCT and should have been replaced by the appropriate SI units. The present expressions should, however, have been retained in parentheses after the replacement expressions.

3.b The use of "and so forth" renders vague the list of examples given at p.7-9. All these expressions should have been deleted from the description.

3.c In case of Entry in the Regional Phase before the EPO, the applicant is reminded that the "incorporation by reference" of not clearly identifiable portions of other documents (such as those at p.8/3 and p.12/8 of the present application) is not according to the practice of the European Patent Office.

Re Item VIII

Certain observations on the international application

4.a It seems that the feature "z = 1 to 2" in claim 9 could be the result of a typing error, the correct feature to be given in claim 9 being instead "z = 0 to 1".

This is suggested by the fact that this feature:

- i) is not supported by any portion of the description,
- ii) is different from the corresponding feature given in claim 1 and at p.3/24 as "z = 0 to 1" and
- iii) is contradicted by claim 10 defining "amine **according to claim 9** wherein z = 0".

4.b If, contrary to expectations, the feature "z = 1 to 2" is really intended in claim 9, then the wording of claim 10 is considered misleading (Article 6 PCT). Formally claim 10 is a claim dependent on claim 9, but the general formula defined in claim 9 does **not** encompass the alternative "z = 0".

In such a case, claim 10 should have been formulated more clearly as an independent claim. For instance by amending "An amine according to claim 9 wherein z = 0." into "An amine according to the formula given in claim 9 **but** wherein z = 0."

4.c It is evident that the "B'" group of the amine of the formula given in claim 9 is the group which after addition to the Si-H group forms the first "B" group mentioned in the formula given for "Q" in claims 1 and 6.

However, while "B" is limited to **not more** than 8 carbons in claims 1 and 6, the amount of C atoms in "B'" is totally **unlimited**.

Moreover, the portion of the description at p.11 mentioning the formula given in present claim 9 defines as "B'" **any alkenyl with "C1-C18"**.

Beside these contradictions, another reason renders **misleading both** the present definitions of "B" and "B'". The symbols "C1 to C8" or "C1 -C18" are normally used to indicate the number of carbon atoms in **continuous hydrocarbon chains** such as in alkanes, alkenes, etc.. and the groups derived therefrom. Similarly, the expression "the alkenyl could be C1-C18" used at p.11/6-8 for "B'" does **not** normally include alkenyl terminated **polyethers**.

Moreover, the fact that B and B' are **hydrocarbon** residues seems confirmed by the use of "B" to indicate **also** the group bridging the N atom to the polyether pendants (i.e. the "B" group in the square brackets): the indication of the polyether block in the square brackets makes only sense if the "B" groups also present in the square brackets **does not** already comprise the possibility of a short polyether block, i.e. if B is intended to indicate **exclusively** an hydrocarbon segment **not containing any ether group**.

On the contrary, it seems evident from p.5/15-18 and p.12/2-8 that **at least** the "B" groups of the modified organopolysiloxane bridging the Si to the N may include also groups wherein the **hydrocarbon chain** is interrupted by "ether bonds".

Therefore, while by reading the claims and most of the description one would expect that the symbols "B" and "B'" can only be **hydrocarbon** bridging groups, by reading the description at p.5/15-18 and p.12/2-8 it is apparent that at least the "B" groups **bridging the Si to the N** and, probably, also "B'" and all the other "B" groups used in the formulae may comprise **ether** bonds.

In conclusion, it seems likely that the **misleading** expressions such as "divalent bridging group of C1 to C8" or "The alkenyl could be C1-C18" and the explicit **contradiction** between:

- the feature "C1-C8" given in claim 1 with respect to the "B" group,

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- the absence of any restriction of the number of carbon atoms given in claim 9 for "B'" and

- the range "C1-C18" given at p.11/7 for "B'",

could be explained by assuming that the applicant has actually intended to define two different alternatives for the "B" group:

a) **any B in any formula may be an hydrocarbon**

b) **the B groups bridging the Si to the N may additionally be an, optionally OH substituted, polyether block with at most 8 carbon atoms obtainable, for instance, from the reaction scheme of D1.**

If this assumption is correct, the applicant should have used a **clearer and more consistent** wording in the **entire application** to express such features.

In particular, the applicant should have avoided the use of the **same symbol** for bridging groups corresponding to **different definitions**, as well as the **contradiction** between the **maximum number of carbon atoms** possibly present in the **reactant portions** and in the **corresponding portions** of the final products.

4.d No "alkenyl" may be a "C1": to form an alkene it is necessary to have 2 carbon atoms. Therefore the expressions "C1 to C18" or "C1 to C6" at p.11/7 should have been amended into, e.g., "up to C18" or "up to C6". Moreover it is not apparent how the methods mentioned in the present application may result in the claimed organosiloxane wherein "B" contains a **single** C atom (see in claims 1 and 6 "...B is a divalent bridging group of C1 to C8..."). The minimum number of C atoms in the "B" group bridging the Si to the N obtainable from the methods mentioned in the present application, as well as in "B'", is **two** carbon atoms. Therefore claims 1 and 6 and the corresponding portions of the description (as well as claim 9, in case the number of carbons of the alkenyl "B'" is specified) should indicate that the "B" group bridging the Si to the N is a divalent bridging group of "up to C8".